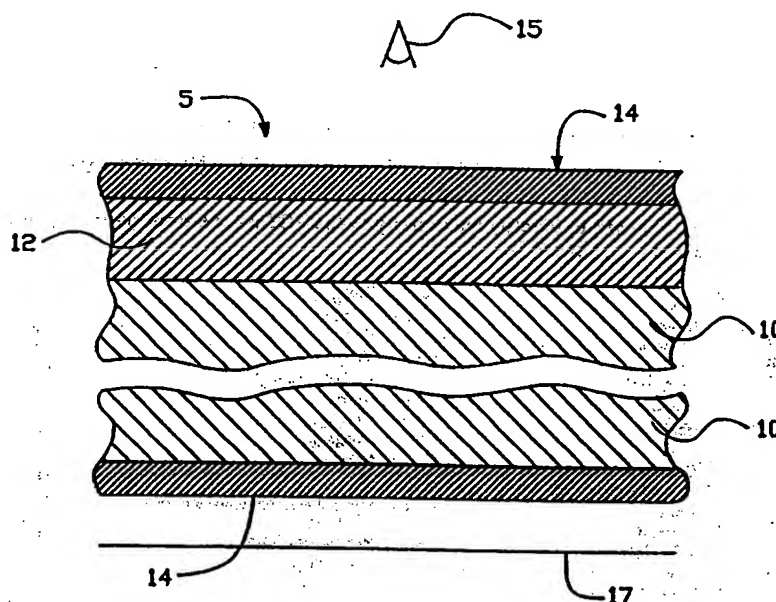




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US91/04998 (22) International Filing Date: 19 July 1991 (19.07.91) (30) Priority data: 557,676                      24 July 1990 (24.07.90)                      US 728,611                      11 July 1991 (11.07.91)                      US (71) Applicant: VIRATEC TRU VUE, INC. [US/US]; 1315 N. North Branch, Chicago, IL 60622 (US). (72) Inventors: STEVENSON, David, E. ; 9124 E. 90th Street, Northfield, MN 55057 (US). TAG, Paul, L. ; 807 Interlaken Drive, Lake Zurich, IL 66047 (US). LAUMANN, Bruce ; 960 62nd Street, La Grange, IL 60525 (US). SCHAEFER, Joy, M. ; 900 W. Devon, Chicago, IL 60660 (US).	(74) Agents: EGAN, William, J., III et al.; Heller, Ehrman, White & McAuliffe, 333 Bush Street, San Francisco, CA 94104-2878 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published With international search report.	

(54) Title: PROTECTIVE GLAZING AND PROCESS FOR MAKING THE SAME



## (57) Abstract

A protective glazing (5) comprising a glass substrate (10) and a resin coating (12) on at least one surface of the substrate. The coating includes an ultraviolet absorbing material and a dye for correcting the transmission color of the substrate (10).

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PROTECTIVE GLAZING AND PROCESS FOR MAKING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates generally to the  
5 prevention of damage due to ultraviolet radiation, and  
more particularly to a protective glazing.

It is well known that fading and color changes  
occur in photographs, paintings, graphic works, and  
other such items when they are exposed to sunlight. It  
10 is also known that fading and color changes can occur as  
a result of exposure to fluorescent light. These  
changes result from chemical changes in the dyes and  
pigments induced by the short wavelength components of  
the light. As such, they may be called photochemical  
15 reactions.

The spectrum of visible light extends from a  
wavelength of about 420 nanometers (nm) to a wavelength  
of about 680 nm. The ultraviolet light spectrum begins  
at wavelengths shorter than about 420 nm and the  
20 infrared light spectrum begins at wavelengths longer  
than about 680 nm. Although most damage may be caused  
by ultraviolet light, some dyes and pigments, such as  
those found in antique watercolors, have a certain

degree of sensitivity to wavelengths at the blue end of the visible spectrum.

Any reduction in exposure to ultraviolet light will help to preserve art or other works. Such measures may include exposing the works only to light from incandescent light sources. Filters designed to remove the damaging wavelengths of light may also be used. An excellent reference on the subject of art conservation is The Museum Environment, Garry Thomson, London Butterworths (1986). Discussions of photochemical degradation are featured on pages 2-17 and 164-193.

While the above mentioned measures may be implemented in a museum environment, they are inconvenient for works which are displayed in the home or office, where the need for a pleasant and comfortable lighting environment often demands illumination by daylight. In this instance, the best solution is to provide protection of the works independent of the lighting environment. This is best done by the use of a suitable protective glazings over the works.

The ideal protective glazing is one in which only the ultraviolet light is rejected while all of the visible light is transmitted. However, a glazing which selectively attenuates certain wavelengths of the visible spectrum and attenuates the ultraviolet light will distort colors and reduce the purity of whites. If blue light is absorbed, such a glazing can impart a yellowish color to objects viewed through the glazing. This is aesthetically unpleasant and is often a reason for not using such glazings as is their additional cost.

Special glasses have been developed to provide rejection of ultraviolet and infrared light. These glasses incorporate cerium oxide in the glass formulation. Examples of such glasses are given in U.S. Patent Nos. 1,536,919; 2,552,125; and 4,792,536.

The spectral transmission characteristics of these glasses are such that the transmission change from essentially zero in the ultraviolet (UV) to about 90 percent in the visible spectrum occurs over a wavelength range of about 70 nm. As a result, the entire range of ultraviolet light can not be rejected without also rejecting at least a portion of the blue light in the visible spectrum. Generally, complete rejection of UV light, without a portion of the blue light also being rejected, can only be accomplished for wavelengths less than about 360 nm. As noted, rejection of a portion of the blue light imparts a yellowish color to objects viewed through a glazing. The above described wavelength range over which the transition from absorption to transmission occurs is often referred to as the ultraviolet absorption edge. The steeper the edge, that is, the shorter the range of transition, the more ultraviolet can be blocked without introducing significant color.

Certain plastic materials have been developed which will reject ultraviolet light and transmit visible light. Such products are sold by the Rohm and Hass Corporation, Philadelphia, PA, under the brand names UF-3 and UF-4. These products are capable of rejecting wavelengths less than about 380 nm. The problem with these materials is that they are soft compared with glass and thus easily scratched. Static charges are also easily built up on their surfaces, and as such, they attract dust. It is also difficult to apply antiglare or antireflection coatings directly to such plastic surfaces. They are also not amenable to etch-type treatments sometimes used to reduce reflection and glare from glass surfaces. Further, thin film type antireflection coatings on plastic are generally not as durable as the same coatings on glass. The plastic

materials which block ultraviolet wavelengths as long as 380 nm also exhibit a slight yellowish transmission color.

The ultraviolet blocking plastics can be laminated with glass sheets to form a composite product that has the durability of glass and also offers ultraviolet rejection properties. This type of laminate glazing is more expensive than conventional glass, requiring more material and labor for its preparation.

10 In view of the foregoing, an object of the present invention is to provide a glazing having a high level of transmission for visible light and a high level of rejection for ultraviolet light.

It is also an object of the present invention to provide a glass glazing that offers ultraviolet rejection properties comparable to the best plastic glazings.

It is another object of the present invention to provide an ultraviolet rejection glazing that is capable of receiving antireflection treatments on one or both surfaces.

It is yet another object of the present invention to provide an ultraviolet rejection glazing that rejects wavelengths up to at least about 380 nm while still providing transmission of visible light at levels comparable to conventional glass of the same thickness.

It is a further object of the present invention to provide a process for making an ultraviolet rejection glass glazing which provides economies of scale, thereby reducing the cost of the glazing.

It is yet another object of the present invention to provide a glass glazing that has color neutral transmission characteristics for visible light.

## SUMMARY OF THE INVENTION

The present invention is directed to a glazing. The glazing comprises a glass substrate having a resin on at least one surface thereof. The resin includes an ultraviolet absorbing material and a dye. The dye is used to correct the transmission color of the substrate.

The glazing may be used to form, for example, a picture framing glass, a display case panel, a vehicle window, or an architectural window or panel. The resin used in the glazing may be a polysiloxane resin. Polysiloxane resins may be abrasion resistant, and may have a high degree of adhesion to glass surfaces.

The coated glazing is essentially as smooth as the uncoated glass substrate. The coating is sufficiently hard that it may be handled and cleaned as in the same manner as glass.

The ultraviolet absorbing material may be an organic compound which can be incorporated into the resin. Such an organic compound may be from the chemical groups benzophenones or benzothiazoles. Up to about 20 percent of such materials can be incorporated into the resin without any substantial loss in hardness or adhesion.

A color-neutralizing dye, or a mixture of dyes, is added to the resin to offset the yellow coloration that would occur as the ultraviolet rejection range is extended closer to the visible light spectrum. The dye color and concentration may be chosen to provide a predetermined neutral color value in combination with the resin and substrate color.

A process for forming the protective glazing may comprise the following steps. A dye for correcting the transmission color may be dispersed in a high boiling point solvent. The solvent, containing the dye, is used to dilute a base resin containing an ultraviolet

absorbing material. The diluted resin can be applied to a substrate using a roll coater. The resin-coated substrate may then be heated to cure the resin.

The solvent may be a glycol having a higher boiling point than any solvent used to formulate the base resin. Such a diluted resin stays wet longer than the base resin. This allows a very uniform coating to be applied. The glycol dilution also permits thickness control over the resin layer to within one tenth of a micron. This enables the ultraviolet blocking and neutral transmission color characteristics to be reproduced precisely from sheet to sheet.

As noted, the dye is added to the solvent before the solvent is added to the base resin. This is more precise and easier to implement than immersing the cured resin in a dye solution.

If the resin is applied to only one surface of a substrate, the other surface may include an antireflection treatment. The resin itself is sufficiently hard and adheres so well to the substrate that it can also be coated with an antireflection coating. The refractive index of the resin should substantially match the refractive index of the substrate so performance of the antireflection coating is not impaired. The coating can be applied economically by in-line sputtering systems such as those used for architectural glass coating.

The antireflection coating reduces reflection from the substrate and increases its transmission. This gain in transmission is more than sufficient to offset the transmission loss caused by the color-correcting dye. This enables a color neutral glass glazing to be made which has enhanced ultraviolet absorbing properties.



The resin once applied to the glass substrate and cured is durable enough to withstand the process conditions of high volume, large area, DC reactive sputtering systems. This provides economies of scale which make protective glazings affordable for the conservation of less expensive graphic works normally seen in the home or office.

#### DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, schematically illustrate a preferred embodiment of the present invention and together with the general description given above and the detailed description of the preferred embodiment given below serve to explain the principles of the invention.

Figure 1A is a schematic representation of a glazing in accordance with the present invention;

Figure 1B is a schematic representation of an antireflection coating in accordance with the present invention;

Figure 2 graphically illustrates the ultraviolet blocking characteristics of glazings in accordance with the present invention;

Figure 3 shows the arrangement of a computer spreadsheet for computing the color coordinates of color correcting dye in accordance with the present invention;

Figure 4 graphically illustrates the method predicting the color coordinates of undiluted color correcting dye;

Figure 5 is a schematic illustration of a roll coater for applying a resin to a substrate in accordance with the present invention; and

Figure 6 graphically illustrates the spectral transmission characteristics of a glazing at various steps in the manufacturing process.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

5       The present invention will be described in terms of a preferred embodiment which is shown in Figures 1A and 1B. As shown, protective glazing 5 includes a glass substrate or sheet 10. The glass substrate may comprise a float glass about 2.5 millimeters (mm) thick. Such  
10       glass is available from Libby Owens Ford (LOF) Glass Inc. of Toledo, Ohio. A resin layer 12 may be disposed on one surface of substrate 10. Alternatively, the resin layer may be formed on both substrate surfaces. An antireflection coating 14 may be disposed on both  
15       resin layer 12 and substrate 10. As illustrated, glazing 5 may be disposed between an observer 15 and, for example, a work of art 17. As noted, the glazing may also be used in vehicles and buildings.

      Resin layer 12 may comprise a polysiloxane resin  
20       of the type described in U.S. Patent No. 4,355,135, the entire disclosure of which is hereby incorporated by reference. Polysiloxane resins are film forming resins containing siloxane bonds alone or in combination with other chemical bonds. The resin layer 12 may be formed  
25       from a base formulation in the form of an aqueous alcoholic dispersion including: (A) about 5 to 75 weight percent, based on the total solids of the base formulation, of colloidal silica; (B) about 0 to 50 weight percent, based on the total solids of the base  
30       formulation, of a partial condensate of a silanol selected from the group of silanols having the formula (i)  $R_w Si(OH)_x$  or (ii)  $R_y Si(OR')_z$  where w, x, y, and z = 2 or 3, and R and R' are organic radicals; (C) about 10 to 55 weight percent, based on the total solids of

the base formulation, of a partial condensate of a silanol having the formula  $R''Si(OR''')_3$  where  $R'''$  is a hydrogen atom or an alkyl radical of 1 to 2 carbon atoms and  $R''$  is an organic radical containing a crosslinking site such as an epoxy, an amine, or an acrylate; (D) about 5 to 10 weight percent, based on the total solids of the base formulation, of a crosslinker, which may be a polycarboxylic acid; and (E) about 1 weight percent, based on the total solids of the base formulation, of a curing catalyst which may be an amine. The components (A), (B), (C), (D), and (E) form what may be termed a base resin composition. The composition may also include about 1 to 20 weight percent, based on the total solids of the base resin composition, of an ultraviolet absorbing material such as a benzophenone, a benzothiazole, or a benzotriazole.

The inclusion of the crosslinker and the curing catalyst in the resin composition speeds the curing of the resin at low temperatures. The above described resin composition may be cured for example at a temperature between about 50°C and 250°C. The curing time is shortened at higher temperatures.

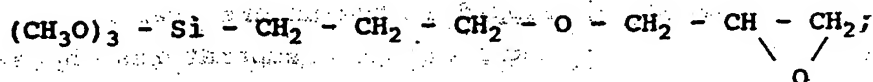
Curing at higher temperatures and consequently shorter times is preferable. The shorter curing time allows the production line to operate faster. The shorter curing time also reduces the probability of quality degradation due to airborne particulates becoming trapped in the uncured resin.

Curing at higher temperatures, however, may also drive a portion of the ultraviolet absorbing material out of the resin composition before the curing is complete. This results in a thicker coating being required to achieve acceptable ultraviolet blocking. It may also result in a shallower ultraviolet absorption edge and a consequently greater tendency to introduce

y llow coloration. Furthermore, as a result of the rapid curing, the ultraviolet absorbing material may not be chemically bound in the cured resin. Under extreme conditions such as boiling in water, the ultraviolet absorbing material may be leached out of the resin coating, reducing its effectiveness as an ultraviolet blocker.

It has been determined that if a high curing temperature of about 200°C is used to cure the resin composition the crosslinker and the curing catalyst may be omitted. It has further been determined that without the crosslinker and the curing catalyst, the ultraviolet absorbing material becomes chemically bonded in the resin composition. The bonding results in a significant reduction in the amount of ultraviolet blocking material lost during curing. Thus a steeper ultraviolet absorbing edge is obtained. Specific examples of resin formulations with and without the crosslinker and the curing catalyst are set forth below.

- 20 In the first example, the resin layer 12 may be formed from a resin composition (W) including:
- (a) about 39 weight percent of colloidal silica;
  - (b) about 16 weight percent of the silanol methyltrimethoxysilane having the formula  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ;
  - 25 (c) about 23 weight percent of the silanol glycidoxypropyltrimethoxysilane having the formula

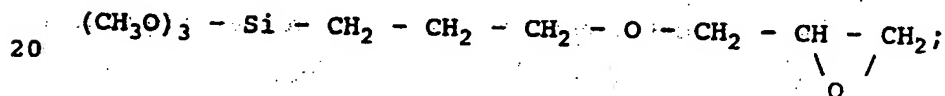


- 30 (d) about 8 weight percent of itaconic acid; (e) about 1 weight percent of benzyldimethylamine; and (d) about 13 weight percent of 2,2',4,4' tetrahydroxybenzophenone. The proportions of the components (a), (b), (c), (d), (e), and (f) are based on the total solids of the resin

composition. Th component (f) provides the ultraviolet blocking or rejecting property of the resin.

Benzophenones, benzothiazoles and benzotriazoles are organic chemical groups that exhibit ultraviolet absorbing or blocking properties. The compounds 2-hydroxy-4-methoxy-benzophenone; 2,4-dihydroxybenzophenone; and 2-(2'-hydroxy-3,5'-di-tert-amylphenyl)benzotriazole have been used successfully. Modifications of the siloxane resin formula may be possible without impairing its capacity to host the ultraviolet blocking agents.

In the second example, the resin layer 12 may be formed from a resin composition (WO) including: (a) about 43 weight percent of colloidal silica; (b) about 17 weight percent of the silanol methyltrimethoxysilane having the formula  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ; (c) about 25 weight percent of the silanol glycidoxypropyltrimethoxysilane having the formula



and (d) about 14 weight percent of 2,2',4,4'-tetrahydroxybenzophenone.

Figure 2 shows the transmission as a function of wavelength for samples of 2mm thick float glass coated with a layer, between about 2 (two) and 3 (three) micrometers thick, of the cured composition (W). (curve A) and a layer between about two (2) and three (3) times of the cured composition (WO) (curve B). The curing temperature for both layers was between about 190 and 210 °C and the curing time for both layers was between about 4 (four) and 5 (five) minutes. The increased steepness of the ultraviolet absorption edge for the

composition without the catalyst and crosslinker is evident.

Figure 1B illustrates an antireflection coating 14 on resin layer 12. The coating 14 on substrate 10 may be identical. The coating 14 may be a multilayer design, including a first film or layer 16 of silicon dioxide ( $\text{SiO}_2$ ) approximately 86 nm thick, a second film 18 of titanium dioxide ( $\text{TiO}_2$ ) approximately 115 nm thick, a third layer 20 of  $\text{SiO}_2$  about 32 nm thick, and a fourth layer 22 of  $\text{TiO}_2$  about 13 nm thick.

As is known, antireflection coating 14 may be applied by DC reactive sputtering in an atmosphere including oxygen. The antireflection coating may be first applied to resin layer 12 and then to substrate 10. The resin formulation should be selected to closely match the refractive index of substrate 10 so that the same antireflection coating can be applied to both the substrate and the resin. This index match also ensures that there are no interference effects between resin layer 12 and substrate 10 which would impair the function of antireflection coating 14.

The resin layer 12 may be applied to the surface of substrate 10 using a roll coater. However, the above-discussed base resin compositions must be modified to facilitate effective application by a roll coater. These base resin compositions may be aqueous alcoholic suspensions of the resin solids. If they are used in this form for roll coating, or even further diluted with an alcohol, they will dry too quickly when spread as a thin layer. This precludes adequate control over layer thickness and the uniformity of that thickness. This lack of control can manifest itself as color variations over a substrate and/or color variations from one substrate to another.

A solvent with a higher boiling point than alcohol should be added to the base resin composition to ensure that it is diluted sufficiently so it remains flowable on the substrate until it is cured. Control of the viscosity of the resin is critical in maintaining control of the thickness of the resin layer and of the uniformity of the thickness over the surface being coated.

The above-discussed resin formulations may be prepared for processing by the roll coater by diluting those compositions with a glycol. The resin formulation may be mixed directly from the constituents in the proportions described above. The resin composition, including a current agent and a catalyst, may also be obtained from a commercial supplier, for example the SDC Corporation of Anaheim, California. The resin may be obtained with or without the ultraviolet blocking additive. The commercial resin may include up to about 25 volume percent, based on the total volume of the resin, of propylene glycol. It was found, however, that this additive was not sufficient, at any degree of dilution, to provide the control of viscosity and flowability demanded for the present invention.

The flowability may be improved by adding to the commercial resin, including the propylene glycol, about 5 to 35 volume percent of hexylene glycol. Superior results, however, may be obtained when the resin formulation includes only hexylene glycol in the proportion of about 5 to 50 percent of the total volume of the resin. The glycol diluent is equally effective in resin compositions with and without a crosslinker and a curing catalyst.

The choice of hexylene glycol as the preferred diluent was made following an extensive period of experimentation on a manufacturing scale. The

experimentation included the testing of many other diluents including: ethyl acetate, propyl acetate, butyl acetate, methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, hexyl alcohol, heptyl alcohol, 5 di-ethyl ether, butyl carbitol, ethylene glycol and propylene glycol. None of these diluents provided satisfactory control of viscosity.

As already discussed, it is believed that the efficacy of the hexylene glycol may be attributed to its 10 high boiling point which helps maintain viscosity during the coating operation. Other solvents than hexylene glycol may provide satisfactory control of viscosity. It is believed, however, that any such solvent should have a boiling point greater than about 189°C, that is, 15 greater than the boiling point of propylene glycol.

The color-correcting or neutralizing dye is dissolved in the hexylene glycol before it is used to dilute the resin. The dye may be a mixture of two or more solvent soluble dyes, for example a cobalt complex 20 dye having the color index number Solvent Red 125 and a copper phthalocyanine dye having the color index number Solvent Blue 67. Solvent Red 125 and Solvent Blue 67 may be obtained from the Ciba Geigy Corporation of Hawthorne, New York under the trade names Orasol Red G 25 and Orasol Blue GN, respectively. Specifically, when the ultraviolet blocking material is 2,2',4,4' tetrahydroxybenzophenone in the proportion of about 13.0 weight percent, the dye mixture may consist of 2.5 parts Orasol Blue GN and 1.0 parts Orasol Red G in the 30 proportion of about 0.0047 weight percent of the total solids of the base resin composition.

The dye is chosen such that it absorbs green and red wavelengths of light perceptibly equal to the amount of blue light absorbed by the ultraviolet-absorbing 35 agent. Thus, the total absorption includes perceptibly



equal amounts of all primary colors. As such, the transmission color through the substrate is substantially neutral.

Generally, as the wavelength of the absorbed ultraviolet light increases, the transmitted light becomes more yellow. If such is the case, more dye must be added to neutralize the yellow color. Quantity of dye required to effect color correction may be between about 0.001 and 0.1 weight percent, based on the total solids of the resin composition. Adding the dye to the glycol additive provides more precise control over the dying operation, as an immersion method would not be suitable for introducing such small quantities of dye.

The specific quantity of dye added may vary widely depending on the type and origin of the dye and its degree of dilution as purchased. A method of determining a suitable dye color and dilution independent of the concentrated dye dilutions will now be described.

Using spreadsheet software such as "EXCEL", available from Microsoft of Redmond, Washington, a worksheet may be set up as shown in Figure 3. In column C1 from row R4 to row R44, wavelength values from 380 to 780 nm are entered at 10 nm intervals. In column C2 from row R4 to row R44, the transmission values, for the appropriate wavelengths, of a glazing coated with a resin without a correcting dye are entered. In column C3 from row R4 to row R44, the values of radiated intensity of a CIE standard illuminant such as illuminant "C" are entered. In columns C4, C5 and C6 from row R4 to row R44, the of the CIE standard observer response values  $\bar{x}$ ,  $\bar{y}$ , and  $\bar{z}$ , respectively, are entered. The calculation of the CIE color coordinates may be accomplished by multiplying in turn the  $\bar{x}$ ,  $\bar{y}$  and  $\bar{z}$  values by the corresponding

transmission and radiated intensity values and entering the results in columns C7, C8, and C9, respectively, from row R4 to row R44. The values in columns C7 rows 4 to 44 are summed in cell C7/R45 (shaded). The sum represents the CIE integral value X. The process is repeated to give the CIE integral values Y and Z in shaded cells C8/R45, and C9/R45 respectively. The X, Y, and Z integral values are summed and entered in cell C7/R46. The CIE color coordinates (x, y, and z), represent the integral values X, Y, and Z as a decimal fraction of the sum of X, Y, and Z. They may be calculated and displayed in column C1 rows R1 to R3 (shaded). The x, y, and z values for the standard illuminant (the neutral point) may be displayed in the shaded cells C2/R1, C2/R2, and C2/R3 to permit a rapid comparison with the coordinates of the glazing.

Once the coordinates of the resin coated glazing without the correcting dye are calculated and displayed, one or more of the tabulated wavelengths between about 500 nanometers and 700 nanometers may be selected. For example some wavelength value representing green, for example 520 nm, and some value representing red, for example 630 nm, may be selected. The transmission values at the selected wavelengths are reduced until the coordinates of the glazing in the shaded cells of column C1 match the coordinates of the illuminant in column C2. If a match can not be obtained when transmission is reduced to zero at the selected wavelength or wavelengths, additional red or green wavelengths may be selected until a match is obtained.

When a satisfactory match has been maintained, color coordinates for the correcting dye may be determined by from the reduced transmission values at the selected wavelengths. For example, the transmission values in the blue region of the spectrum, that is at

wavelengths less than about 500 nm, may be set to equal to the highest values of transmission in the spectrum of the glazing. The transmission values at wavelengths less 500 nm are strongly influenced by absorption in the ultraviolet absorbing material in the resin. Setting such transmission values equal to the highest values in the spectrum thus produces the effect of removing the ultraviolet absorbing material from the resin. That which remains is equivalent to the glazing coated with a resin containing only a correcting dye. The coordinates in column C1 now represent the "dye" that has been created by the selected reduction of red and green wavelengths. Any real dye which has the computed color coordinates can be used to make the color correction with that particular resin. The transmission spectrum of that dye may be different from the transmission versus wavelength values represented on the spreadsheet. Dye color coordinates calculated according to the above procedure will be very close to the neutral point. The actual hue represented by the coordinates would, in practice, be very difficult to judge by eye. This is because of its proximity to the neutral point. A procedure for determining a practical dye mixture is as follows:

The dye color coordinates calculated according to the above procedure are plotted on a CIE coordinate diagram along with the coordinates of the illuminant or neutral point. This is illustrated in Figure 4. The point CN represents the coordinates of the standard illuminant ("C") or the neutral point and the point CU represents the coordinates of the correcting dye. A straight line LC is drawn between neutral point CN and dye point CU. Any set of coordinates lying on line LC will represent to an adequate approximation a dye having the same hue but different color saturations. A color

represented by point CS is very saturated and the hue is readily distinguishable by eye from adjacent hues on the CIE diagram.

A concentrated dye of the correct hue may be prepared by mixing a red dye and a blue dye in a container and matching the color against a sample known to have coordinates lying on line LD. A more accurate technique is to employ a colorimeter such as the "Hunterlab Ultrascan Colorimeter", available from Hunter

10 Associates Laboratory of Reston Virginia. The concentrated dyes may be mixed in a sample cell, and proportions of red and blue adjusted until the color coordinates of the dye in the cell, measured on the colorimeter fall on line LD. The concentrated dye mixture may then be diluted with a neutral colored solvent until the measured coordinates match the actual dye point CU. Thus, the dye mixture proportions and the dilution level required to effect a proper color correction may be established.

20 A process for forming a protective glazing in accordance with the present invention will now be described. The glass substrate 10 to be coated is first washed using a flat glass washer available from Bilco Inc. of New Haven, Connecticut. Such washers are typically used in the glass processing industry and can be purchased as a complete system. The washing system comprises two washers and a rinse unit. The glass sheet or substrate passes through the washers where it is washed with hot demineralized water, and then rinsed with deionized (DI) water. It then may be dried with a multiple air knife system and transferred by conveyor to a roll coater.

The roll coater may a Model 300 supplied by Black Brothers of Mendota, Illinois. The roll coater is configured for forward roll application to the top

surface of the substrate as the substrate travels horizontally through the coater. The principle of the coater operation is illustrated by Figure 5.

The roll coat r includes a fluid reservoir (not shown), containing 45 gallons of the diluted resin, i.e. diluted with the glycol containing the color-correcting dye. This resin formulation is metered from the fluid reservoir into space 30 between rollers 32 and 34.

Roller 32 is the coating roller, and roller 34 is the doctor roller. A pool 36 is formed between and extends along the length of the rollers. A guard 31 covers space 30 between the rollers to prevent foreign objects or particles from entering or being caught in that space.

15 The substrate 10 is supported by rollers 40 and driven in the direction of Arrow A by roller 42. Roller 42 rotates in the direction of Arrow B and coating roller 32 rotates in the direction of Arrow C. Rollers 32 and 42 may rotate at an angular velocity of about 30 revolutions per minute (rpm). The rollers 32 and 40 may each have a diameter of about 9 inches. The diameters and angular velocities of the rollers translate to a line speed for substrate 10 of about 75 feet per minute. The roller 34 is rotated in the direction of Arrow D. 25 Its peripheral speed is about one-twentieth of the peripheral speed of roller 32. The shear force set up by this speed differential ensures that coating 44 is transferred primarily to the surface of roller 32 and from there to substrate 10.

30 All the rollers may be surfaced with a 40 Durometer EPDM rubber. The above-described roll coater will accept glass sheets up to 50 inches in width.

Excess coating or resin material spills out of the space (not shown) at the ends of rollers 32 and 34.

35 This excess material is collected in a trough (also not

shown) below the rollers. The thickness control for layer 44 is effected by varying the peripheral speed of roller 34 and the pressure of roller 34 on roller 32.

The diluted resin may be rolled onto glass sheet 10 at a temperature of about 20°C. The thickness of layer 44 may be about 7.5 micrometers.

The thickness of the resin layer is chosen to provide optimum ultraviolet blocking consistent with maintaining the smoothness of the finished glass. It has been determined that the smoothness of the original glass surface may be maintained if the cured resin thickness is less than about 8 micrometers. It is difficult to maintain thickness control and uniformity if the thickness of the cured resin exceeds about 8 micrometers.

After the above-described steps, substrate 10 is transferred by conveyor to a curing oven. The curing temperature may be between about 50°C and 250°C. The curing times are adjusted according to the curing temperature. Preferably, the resin-coated substrate is baked for about 4 minutes at a temperature of about 200°C. After the curing step, the resin is fully hardened. The thickness of the resin layer after hardening may be about 2.5 micrometers.

Using the above-described process, substrates may be coated using resin formulations from which the crosslinker and curing catalyst are omitted. This may be possible because of the high curing temperature of about 200°C.

Steps are taken in the process described above to minimize particulate contamination of the resin coating. For example, the process may be carried out inside a Class 100 clean room enclosure. This includes the transfer of the substrates from the washers to the coater and from the coater to the curing oven. The oven

itself is operated with a flowing filtered air supply and a positive pressure designed to maintain the interior in a Class 100 condition.

A resin management system (not shown) should  
5 include a filtering system to extract particulates from the diluted resin. This system may comprise a 1 micron prefilter and a 0.4 micron absolute filter. Excess resin which results from the thickness control process described above is pumped, using a two stage diaphragm  
10 pump, through the filtering system and then returned to the fluid reservoir. This aspect of the process reduces waste as well as manufacturing costs.

While these particulate management steps are not an essential part of the invention, as far as the  
15 ultraviolet blocking properties of the glazing are concerned, they do illustrate measures which will improve the overall quality of the resin-coated glazing. Other such measures will be evident to those skilled in the art.

20 The ability to use a fast, high-volume coater for resin coating allows the resin-coated glazing to be cost competitive with the ultraviolet blocking plastic materials described above.

Figure 6 shows the spectral performance of a  
25 glass glazing at different stages of the fabrication process. Curve C represents a transmission versus wavelength plot for an untreated glass sheet or substrate. Curve D is a transmission versus wavelength plot for the sheet plus a resin coating applied using  
30 the above-described process. Curve E shows the transmission of the finished glazing according to the construction of Figure 1A. The visible spectral range is the range V extending from the blue limit of

visibility VB (at about 420 nm) to the red limit of visibility VR (at about 680 nm).

The effectiveness of the color-neutralizing or correcting dye is evident from the slight drop in transmission in the yellow-green region G and the red region R. As can be seen, the dye causes a perceptibly equal loss of transmission of the red and green wavelengths to match the loss of transmission of the blue wavelengths between VB and a wavelength of about 450 nm.

The color-neutralizing dye plus the ultraviolet absorbing material remove perceptibly equal proportions of the three primary colors from the light transmitted through the substrate. The transmission color is, therefore, color neutral as opposed to yellow had the dye not been used. The total loss in visible light transmission resulting from the blue absorption and the dye color correction is approximately 4 percent. This can be seen by the transmission differences between Curves C and D (Figure 6). Through the use of antireflection coatings, which reduce the surface reflections of the resin and the glass from about 9.0 percent to less than 0.5 percent without introducing further absorption, the finished product (See Curve E) has a higher total transmission than the uncoated glass.

As discussed above, the amount and composition of dye is determined by the transmission loss of blue light caused by the ultraviolet absorbing material. If the ultraviolet absorption were at sufficiently short wavelengths, the dye may not be needed.

Another embodiment of the present invention includes providing the ultraviolet blocking property of the resin by using inorganic materials, such as cerium oxide, titanium oxide, neodymium oxide, and zinc oxide.



The oxide materials may be introduced into the polysiloxan resins in the form of a colloidal suspension. Up to 15 percent weight of cerium dioxide may be introduced into the resin in this way. When colloidal suspensions of ultraviolet blocking oxides are used, the amount of colloidal silica used may be correspondingly reduced. Organic ultraviolet blocking materials may be omitted from the resin if inorganic ultraviolet blocking materials are used.

10 A general form of the base resin formulation using inorganic blocking materials would be an aqueous alcoholic dispersion including: (A) about 5 to 70 weight percent, based on the total solids of the base formulation, of colloidal silica; (B) about 5 to 15 weight percent, based on the total solids of the base formulation, of an inorganic ultraviolet blocking material in colloidal form; (C) about 0 to 50 weight percent, based on the total solids of the base formulation, of a partial condensate of silanol having the formula (i)  $R_w Si(OH)_x$  or (ii)  $R_y Si(OR')_z$ , where w, x, y and z = 2 or 3, and R and R' are organic radicals; (D) about 10 to 55 weight percent, based on the total solids of the base formulation, of a partial condensate of a silanol having the formula  $R''(OR''')_3$ , where R''' is a hydrogen atom at an alkyl radical of 1 to 2 carbon atoms and R'' is an organic radical containing a crosslinking site such as an epoxy, an amine or an acrylate; (E) about 5 to 10 weight percent, based on the total solids of the base formulation, of a crosslinker, which may be a polycarboxylic acid; and (F) about 1 weight percent, based on the total solids of the base formulation, of a curing catalyst which may be an amine.

25 A resin-coated glazing about 7.7 micrometers thick and containing 6 weight percent, based on the total solids of the base formulation, of cerium oxide

provides complete blocking of ultraviolet wavelengths shorter than about 365 nm. The resin composition having the inorganic blocking material may be formulated without a crosslinker and a curing catalyst if the curing temperature is about 200°C.

The foregoing discussions have involved polysiloxane resins. Other resins, of course, may be formulated to include ultraviolet blocking materials and color correcting dye. Such resins may include, for example, acrylics, methacrylates and melamines. As already discussed, polysiloxane resins are preferred because they have excellent adhesion to glass and may have hardness comparable to glass.

Certain other product and process variations will be immediately evident to those skilled in this art. For example, it should be apparent that various other antireflection coatings could be used. The coatings could have more layers or fewer layers, and be made from various materials. Such coatings could be applied by thermal evaporation techniques provided the temperature of the resin-coated glass was not allowed to rise above about 260°C during the deposition process.

It is also possible to provide an antireflection coating by chemical treatments as, for example, described in U.S. Patent No. 2,490,662. Here, a film having a lower refractive index than the glass is formed on the glass by selective chemical removal of certain components of the glass.

The glass substrate may also be chemically etched to form a light diffusing surface. This procedure, however, while reducing surface reflection, does not provide an increase in transmission.

The present invention has been described in terms of a preferred embodiment. The invention, however, is not limited to the embodiment described and depicted.

Rather, the scope of the invention is limited by the appended claims.

WHAT IS CLAIMED IS:

1. A glazing, comprising:  
a glass substrate and on at least one surface thereof a resin including an ultraviolet light absorbing material and a dye for correcting the transmission color of said glazing.
2. The glazing of Claim 1 wherein said resin is selected from the group consisting of acrylics, methacrylates, and melamines.
3. The glazing of Claim 1 wherein said resin is a polysiloxane resin.
4. The glazing of Claim 3 wherein said resin is formed from a composition including: (a) a base resin comprising (i) about 5 to 75 weight percent, based on the total solids of (a), of colloidal silica; (ii) about 0 to 50 weight percent, based on the total solids of (a), of a partial condensate of a silanol selected from the group of silanols having the formula  $R_wSi(OH)_x$  or  $R_ySi(OR')_z$  where  $w, x, y,$  and  $z = 2$  or  $3$ , and  $R$  and  $R'$  are organic radicals; and (iii) about 10 to 55 weight percent, based on the total solids of (a), of a partial condensate of a silanol having the formula  $R''Si(OR''')_3$  where  $R'''$  is a hydrogen atom or an alkyl radical of 1 to 2 carbon atoms and  $R''$  is an organic radical containing a crosslinking site; (b) about 1 to 20 weight percent, based on the total solids of (a), of said ultraviolet absorbing material; and (c) about 5 to 50 percent by volume, based on the volume of said composition, of a solvent having a boiling point greater than about 189°C for controlling the viscosity of the composition.

5. The glazing of Claim 4 wherein said dye is included in said solvent.

6. The glazing of Claim 5 wherein said ultraviolet absorbing material is selected from a group consisting of benzophenones, benzothiazoles and benzotriazoles.

7. The glazing of Claim 5 wherein said solvent includes at least a glycol.

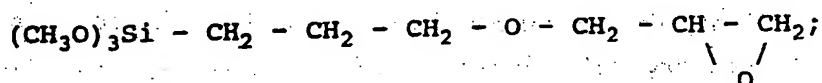
8. The glazing of Claim 3 wherein said resin is formed from a composition including: (a) a base resin comprising (i) about 5 to 75 weight percent, based on the total solids of (a), of colloidal silica; (ii) about 0 to 50 weight percent, based on the total solids of (a), of a partial condensate of a silanol selected from the group of silanols having the formula  $R_wSi(OH)_x$  or  $R_ySi(OR')_z$  where  $w$ ,  $x$ ,  $y$ , and  $z = 2$  or  $3$ , and  $R$  and  $R'$  are organic radicals; and (iii) about 10 to 55 weight percent, based on the total solids of (a), of a partial condensate of a silanol having the formula  $R''Si(OR'')_3$  where  $R''$  is a hydrogen atom or an alkyl radical of 1 to 2 carbon atoms and  $R''$  is an organic radical containing a crosslinking site; (b) a crosslinker for (a); (c) a curing catalyst; (d) about 1 to 20 weight percent, based on the total solids of (a), of said ultraviolet absorbing material; and (e) about 5 to 50 percent by volume, based on the volume of said composition, of a solvent having a boiling point greater than about 189°C for controlling the viscosity of the composition.

9. The glazing of Claim 8 wherein said dye is included in said solvent.

10. The glazing of Claim 9 wherein said ultraviolet absorbing material is selected from a group consisting of benzophenones, benzothiazoles and benzotriazoles.

5 11. The glazing of Claim 9 wherein said solvent includes at least a glycol.

12. The glazing of Claim 1 wherein said resin is formed from a composition including: (a) about 39 weight percent, based on the total solids of said composition, of colloidal silica; (b) about 16 weight percent, based on the total solids of said composition, of a partial condensate of a silanol having the formula  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$  and about 23 weight percent, based on the total solids of said composition, of a partial condensate of a  
15 silanol having the formula



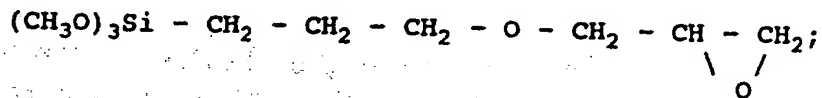
(c) about 14 weight percent, based on the total solids  
20 of said composition, of said ultraviolet absorbing material; and (d) about 5 to 50 percent by volume, based on the volume of said composition, of a solvent having a boiling point greater than about 189°C.

13. The glazing of Claim 12 wherein said  
25 ultraviolet absorbing material is 2, 2', 4, 4' tetrahydroxybenzophenone.

14. The glazing of Claim 13 wherein said solvent is hexylene glycol.

15. The glazing of Claim 14 wherein said dye is a mixture of 2.5 parts blue dye and 1 part red dye.

16. The glazing of Claim 1 wherein said resin is formed from a composition including: (a) about 39 weight percent, based on the total solids of said composition, of colloidal silica; (b) about 16 weight percent, based on the total solids of said composition, of a partial condensate of a silanol having the formula  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$  and about 23 weight percent, based on the total solids of said composition, of a partial condensate of a silanol having the formula



(c) about 8 weight percent, based on the total solids of said composition, of a crosslinker (d) about 1 weight percent, based on the total solids of said composition, of a curing catalyst; (e) about 13 weight percent, based on the total solids of said composition, of said ultraviolet absorbing material; (f) about 5 to 50 percent by volume, based on the volume of said composition, of a solvent having a boiling point greater than about 189°C; and (g) about 0.0047 weight percent, based on the total solids of said composition, of said dye.

17. The glazing of Claim 16 wherein said ultraviolet absorbing material is 2, 2', 4, 4' tetrahydroxybenzophenone.

18. The glazing of Claim 17 wherein said solvent is hexylene glycol.

19. The glazing of Claim 18 wherein said dye is a mixture of 2.5 parts blue dye and 1 part red dye.

20. The glazing of Claim 1, 4, 8, 12, or 16 further including means for reducing reflection from at least one surface of said substrate.

21. The glazing of Claim 20 wherein said reflection reducing means includes a light diffusing surface.

22. The glazing of Claim 20 wherein said reflection reducing means includes a surface film having a lower refractive index than said substrate.

23. The glazing of Claim 22 wherein said surface film is formed on a surface of said substrate opposite from the surface on which said resin is disposed.

24. The glazing of Claim 20 wherein said reflection reducing means includes a plurality of thin films.

25. The glazing of Claim 1 wherein said resin is formed from a composition including: (a) a base resin comprising (i) about 5 to 70 percent weight, based on the total solids of (a), of colloidal silica; (ii) about 5 to 15 weight percent, based on the total solids of (a), of an inorganic ultraviolet absorbing material; (iii) about 0 to 50 weight percent, based on the total solids of (a), of a partial condensate of a silanol selected from the group of silanols having the formula  $R_wSi(OH)_x$  or  $R_ySi(OR')_z$  where  $w$ ,  $x$ ,  $y$ , and  $z$  = 2 or 3, and  $R$  and  $R'$  are organic radicals; and (iv) about 10 to 55 weight percent, based on the total solids of (a), of



a partial condensate of a silanol having the formula  $R''Si(OR'')_3$  where  $R''$  is a hydrogen atom or an alkyl radical of 1 to 2 carbon atoms and  $R''$  is an organic radical containing a crosslinking site; (b) about 5 to 50 percent volume, based on the volume of said composition, of a solvent having a boiling point greater than about 189°C; and (c) about 0.001 to 0.05 percent weight based on the total solids of (a) of said dye.

26. The glazing of Claim 1 wherein said resin is formed from a composition including: (a) a base resin comprising (i) about 5 to 70 percent weight, based on the total solids of (a), of colloidal silica; (ii) about 5 to 15 weight percent, based on the total solids of (a), of an inorganic ultraviolet absorbing material; (iii) about 0 to 50 weight percent, based on the total solids of (a), of a partial condensate of a silanol selected from the group of silanols having the formula  $R_wSi(OH)_x$  or  $R_ySi(OR')_z$  where  $w$ ,  $x$ ,  $y$ , and  $z = 2$  or  $3$ , and  $R$  and  $R'$  are organic radicals; and (iv) about 10 to 55 weight percent, based on the total solids of (a), of a partial condensate of a silanol having the formula  $R''Si(OR'')_3$  where  $R''$  is a hydrogen atom or an alkyl radical of 1 to 2 carbon atoms and  $R''$  is an organic radical containing a crosslinking site; (b) a crosslinker for (a); (c) a curing catalyst; (d) about 5 to 50 percent volume, based on the volume of said composition, of a solvent having a boiling point greater than about 189°C; and (e) about 0.001 to 0.05 percent weight based on the total solids of (a) of said dye.

27. The glazing of Claim 1 forming a picture frame glass.

28. The glazing of Claim 1 forming a panel for a display case.

29. The glazing of Claim 1 forming a window for a vehicle.

5 30. The glazing of Claim 1 forming a window for a vehicle.

31. A glazing, comprising a glass substrate having a polysiloxane resin on a first surface thereof, said resin including an ultraviolet absorbing material and a dye for correcting the transmission color of the glazing, and an antireflection coating formed on an exterior facing surface of said resin and on a second surface of said substrate.

15 32. A process for coating a glass substrate with a resin having an ultraviolet light absorbing material incorporated therein, comprising: mixing with the resin a solvent having a boiling point greater than 189°C to form a coating composition; applying by a roll coater said coating composition to the substrate to form a layer thereon; and curing said layer at a temperature between about 50°C and 250°C.

33. The process of Claim 32 wherein said solvent includes a dye for correcting the transmission color of the resin coated substrate.

25 34. The process of Claim 33 wherein said dye comprises about 2.5 parts blue dye and 1 part red dye.

35. The process of Claim 32 or 33 wherein said solvent includes at least one glycol.

36. The process of Claim 35 wherein said glycol is hexylene glycol.

5 37. The process of Claim 32 wherein said ultraviolet absorbing material is selected from the group consisting of benzotriazoles, benzophenones and benzothiazoles.

38. The process of Claim 33 wherein said dye is  
10 formulated by a process including:

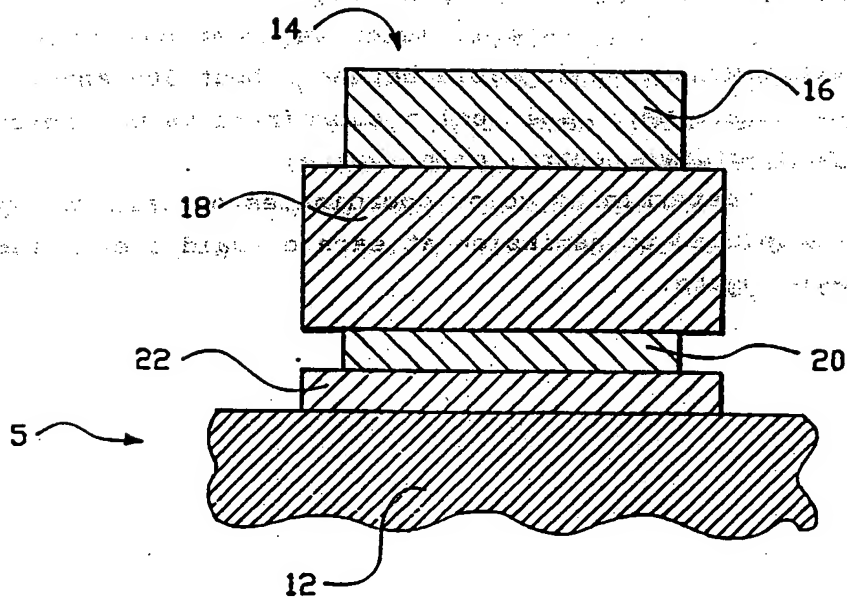
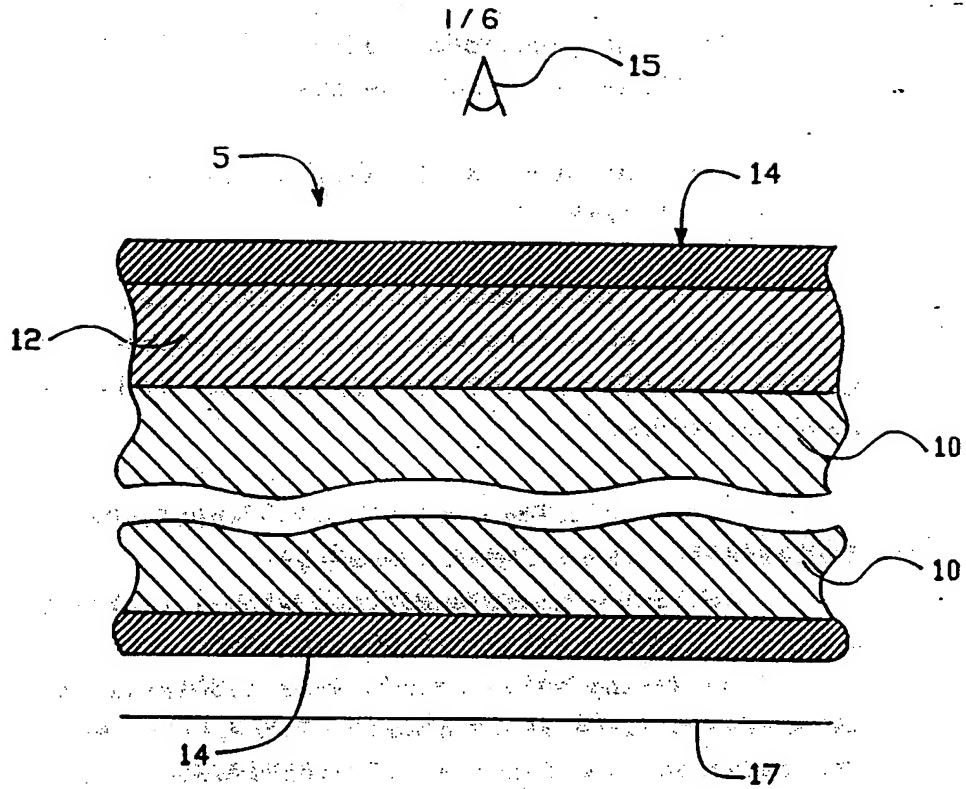
coating a glass substrate with a layer of said resin to form a resin coated substrate;

measuring said resin coated substrate to  
determine to determine values of visible light  
15 transmission as a function of wavelength;

entering said values of transmission as a function of wavelength in a table to enable color coordinate values to be calculated;

reducing a transmission value at one or more  
20 wavelengths in said table between about 500 and 700 nanometers until said color coordinate values reach a predetermined neutral point value;

determining color coordinates of said dye from the reduced transmission at each of said one or more  
25 wavelengths.



**SUBSTITUTE SHEET**

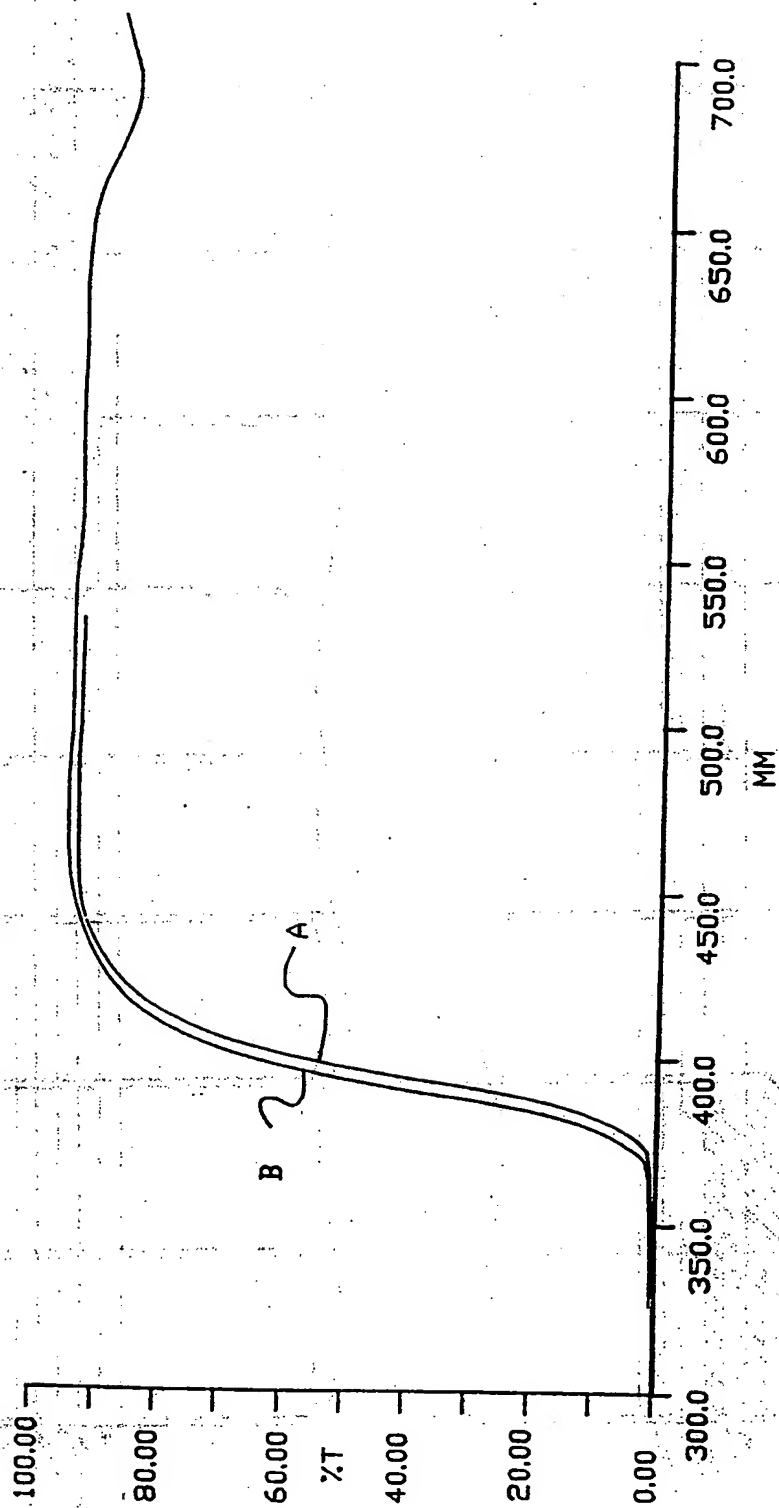


FIG.-2

SUBSTITUTE SHEET

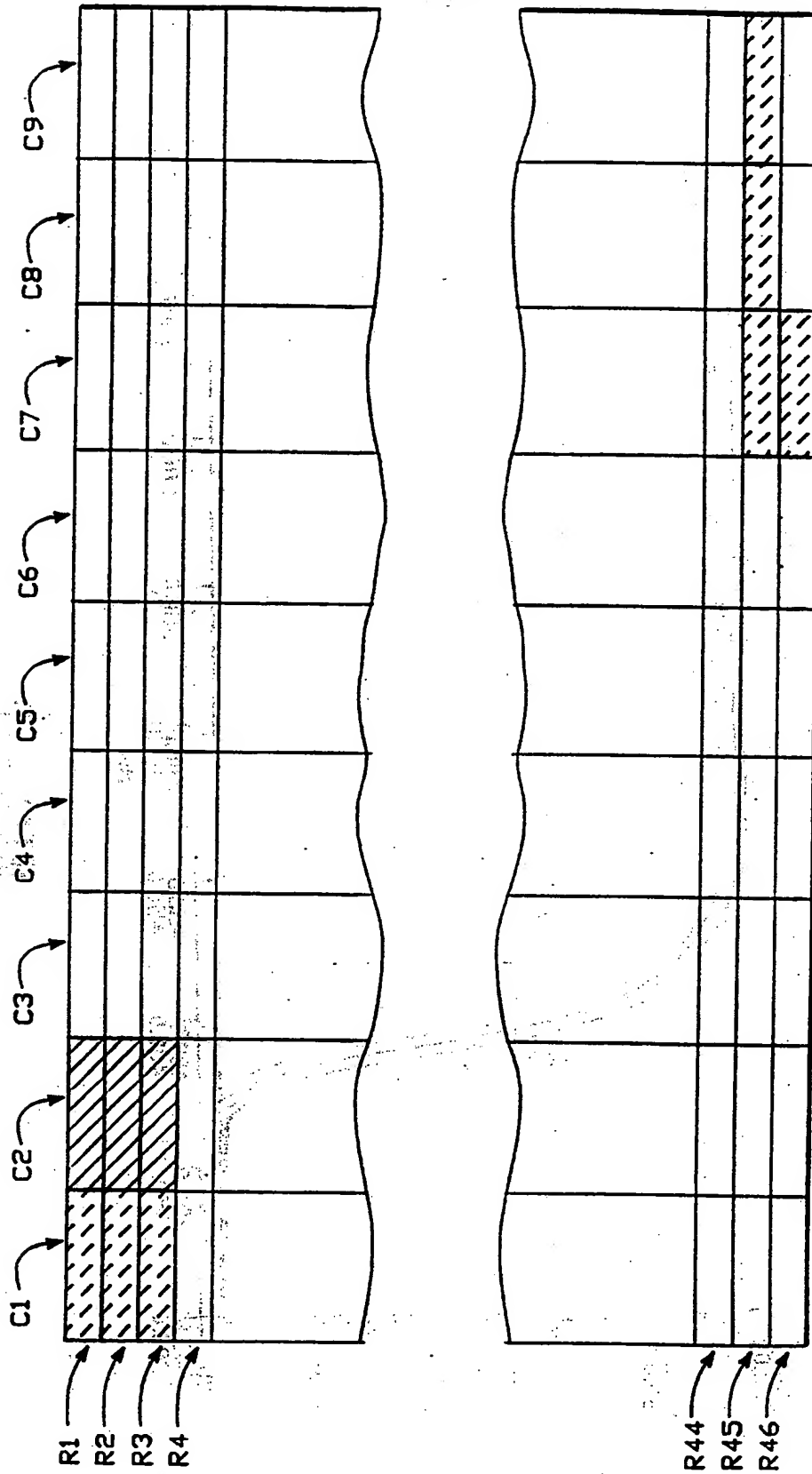


FIG.-3

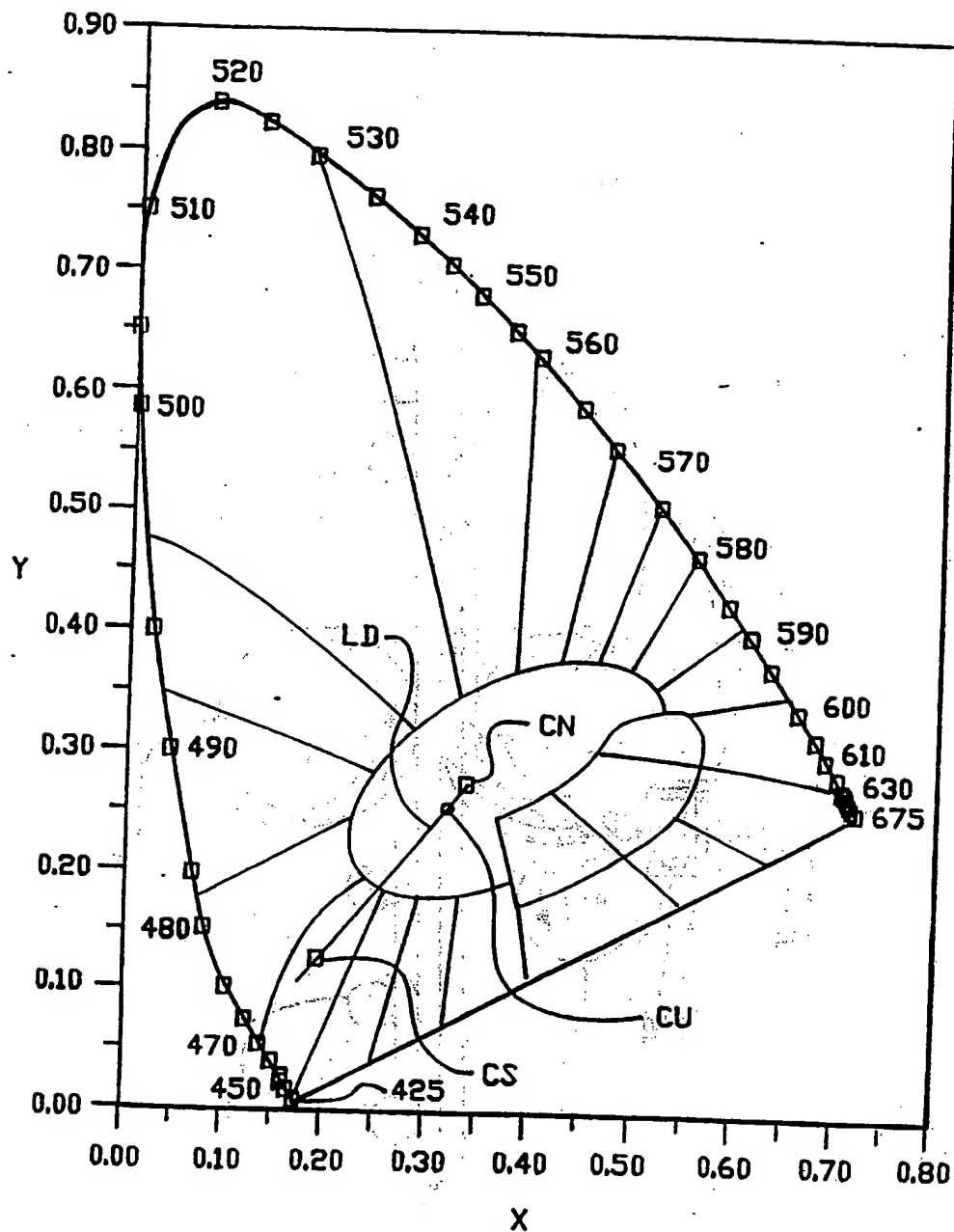


FIG.-4

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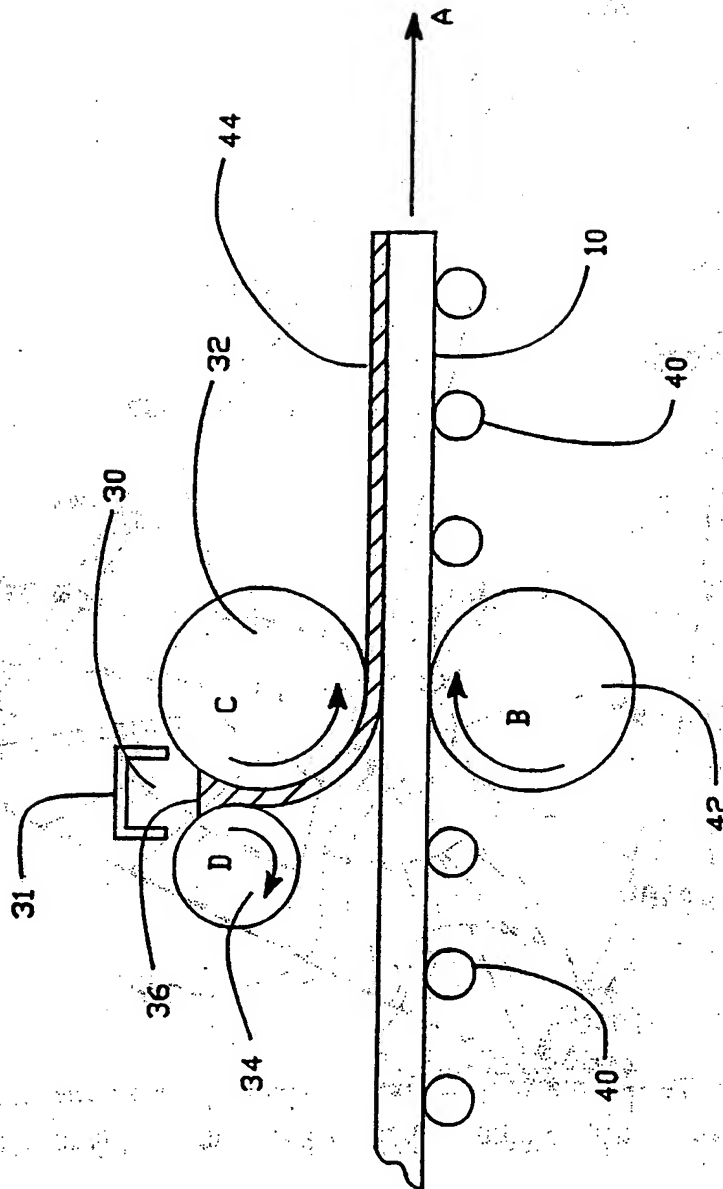


FIG.-5

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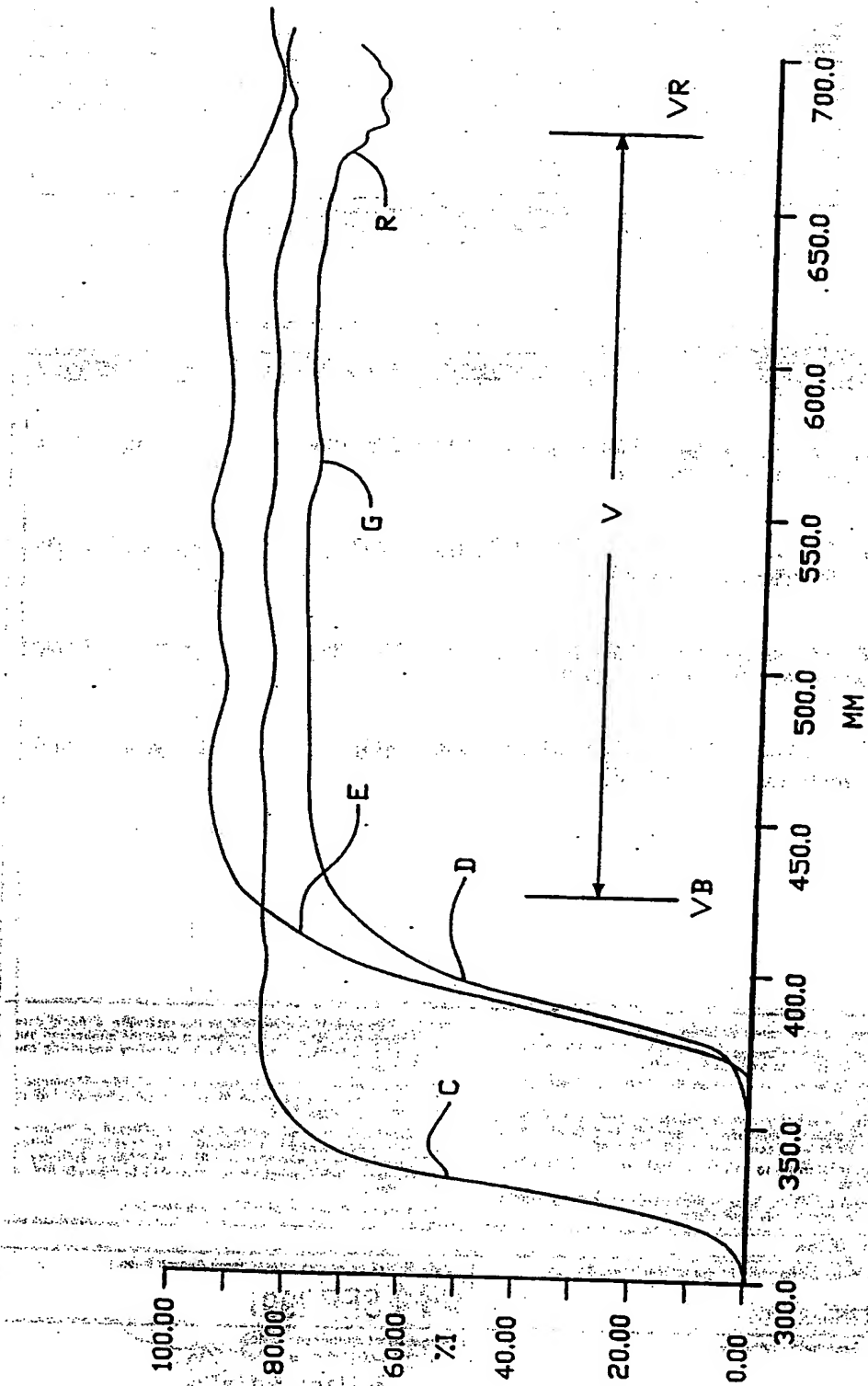


FIG.-6

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